Biologically Labile and Refractory Phosphorus Loads from the Agriculturally-Managed Upper Eau Galle River Watershed, Wisconsin

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Abstract

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Fractionation techniques were used to quantify various biologically labile (*i.e.*, directly available for biological uptake or subject to recycling pathways) and refractory (*i.e.*, biologically unavailable and subject to burial) particulate and soluble phosphorus (P) forms along the longitudinal axis of the agriculturally-managed Upper Eau Galle River watershed in west-central Wisconsin. P loading increased as a function of increasing distance from the river's headwaters. However, areal P export rates were similar longitudinally, indicating a relatively homogeneous land-use mosaic throughout the watershed. P loads were composed of predominantly biologically labile constituents (*i.e.*, 79%), with soluble P forms (*i.e.*, soluble reactive and unreactive P) accounting for 49% and labile particulate P forms (*i.e.*, loosely-bound PP, iron-bound PP, and labile organic/polyphosphate PP) accounting for 30% of the P load. Soluble P forms are either directly available for biological uptake or can be converted to available forms through enzymatic (*i.e.*, alkaline phosphatase) reactions. Deposition and retention of loosely-bound and iron-bound PP in the receiving impoundment, Eau Galle Reservoir, can become an important source of internal P loading via eH and pH chemical reactions. Suspended solids loads also exhibited a high equilibrium P concentration (*i.e.*, EPC > 0.10 mg L⁻¹) that was similar to flow-weighted soluble reactive P concentrations in the river, suggesting equilibrium control of soluble P as loads entered the reservoir. The high EPC and a linear adsorption coefficient approaching 1000 L kg⁻¹ indicated that binding sites of eroded soils in the runoff were enriched with P due to soil nutrient management. Our results indicated that transformations, transport, and fate of biologically labile PP, as well as soluble P, need to be considered in load reduction management to eutrophic receiving waters.

Key Words: Adsorption-desorption, biological phosphorus availability, equilibrium phosphorus concentration, labile phosphorus forms, loading, phosphorus, refractory phosphorus forms, runoff, watershed

Excessive nutrient runoff (usually as phosphorus) in agriculturally-managed watersheds is a primary cause for eutrophication of phosphorus-limited receiving waters. Because agricultural soils are often managed for crop uptake of nitrogen (N) rather than phosphorus (P), additions of fertilizers and manures can result in the buildup of soil P that exceeds crop requirements. The excess can be transported to receiving waters during runoff (Lemunyon and Gilbert 1993; Sharpley et al. 1994; Sharpley 1995). In addition, watersheds managed for livestock (such as dairy operations) rely on frequent manure applications to the soil. This practice results in the buildup of excessive P levels in soils due to the low N:P ratio of manures versus crop uptake N:P ratio requirements (Gburek et al. 2000). Simulation of P runoff via modeling is critical for the development of management scenarios to control excessive P runoff from agriculturallymanaged watersheds. However, algorithms need to address transformation, transport, and fate of biologically labile P

forms in order to more accurately predict biological response to loads entering receiving waters.

Basic total and soluble phosphorus watershed loading information does not always accurately reflect biological availability (Sharpley *et al.* 1991; James *et al.* 2002a) and can lead to inaccurate predictions of biological response to P loading in receiving waters (DePinto *et al.* 1986; Auer *et al.* 1998; Chapra and Auer 1999; Schelske *et al.* 1999). Soluble P forms are generally available for biological uptake and assay and chemical extraction procedures have been used to distinguish particulate P (PP) that is directly available for algal uptake and growth (USEPA 1971, Sharpley *et al.* 1991; Sharpley 1993). However, other forms of PP in runoff can become indirectly available for algal uptake and growth via recycling pathways after deposition in receiving waters. For instance, metal hydroxides associated with particulate runoff can be important in P kinetic and equilibrium reactions that

Table 1.-Operationally-defined particulate phosphorus (PP) fractions. Biologically labile = Subject to recycling pathways or direct availability to the biota. Biologically refractory = Low biological availability and subject to burial.

Variable	Extractant	Biological availability and susceptibility to recycling pathways
Loosely-bound PP	1 M ammonium chloride	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Iron-bound PP	0.11 M sodium bicarbonate-dithionate	Biologically labile; available for uptake and can be recycled via eH and pH reactions and equilibrium processes.
Aluminum-bound PP	0.1 N sodium hydroxide	Biologically refractory; generally unavailable for biological use and subject to burial.
Calcium-bound PP	0.5 N hydrochloric acid	Biologically refractory; generally unavailable for biological use and subject to burial.
Labile organic/ polyphosphate PP	Persulfate digestion of the NaOH extraction	Biologically labile; recycled via bacterial mineralization of organic P and mobilization of polyphosphates stored in cells.
Refractory organic PP	Persulfate digestion of remaining particulate P	Biologically refractory; generally unavailable for biological use and subject to burial.

impact biological availability through adsorption or desorption under conditions of P disequilibrium (McDowell et al. 2001; McDowell and Sharpley 2003; James and Barko 2004). Sedimentation of adsorbed P in receiving waters can lead to later recycling via eH and pH reactions at the sediment-water interface (James et al. 1995, 1996). Accreted watershed P can also be recycled by aquatic plants through root uptake and senescence and become a source to algal productivity (James et al. 2002b). These and other recycling pathways, referred to as internal P loads (Cooke et al. 1977), can sustain algal productivity in receiving waters for many years, even when external P loads are reduced through management and rehabilitation technologies.

Our objectives were to use P fractionation techniques to identify and quantify various biologically labile (*i.e.*, directly available for biological uptake or recyclable via biological and chemical transformations) and refractory (*i.e.*, generally unavailable for biological uptake and subject to permanent burial) species of P (Table 1) in loads of the Upper Eau Galle River watershed, west-central Wisconsin. This information was used to identify and quantify the biological reactivity of watershed P loads to the eutrophic Eau Galle Reservoir, for future load reduction management.

Methods

The Upper Eau Galle River basin drains a 123.3 km² watershed above the Eau Galle Reservoir, a U.S. Army Corps of Engineers impoundment located in west-central Wisconsin (Figure 1). Carr Creek is the largest higher order tributary

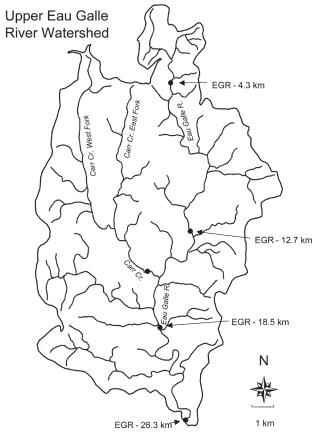


Figure 1.-Map of the Upper Eau Galle River watershed above 26.3 river kilometers showing major tributaries. Solid circles indicate sampling and flow gauging stations.

draining into the Upper Eau Galle River with a watershed size of 35 km² (*i.e.*, 28% of the entire Upper Eau Galle River watershed). Agricultural land-uses are dominated by annual and perennial crop production (*i.e.*, corn, oats, alfalfa, grass hay, soy beans), pasture, and livestock dairy production. Other land-uses include CRP (Conservation Reserve Program) and wooded areas. Other than one small town (Woodville; population = 1100) located near the approximate center of the watershed, the residential distribution is sparse and rural. Overall, agricultural land uses comprise 93% of the watershed area; versus 2% for urban/residential settings and 5% for woodlands.

The watershed is located within the glaciated region of Wisconsin and the dominant soil associations are the Vlasaty-Skyberg, located in the eastern portion of the watershed, and Saltre-Pillot Antigo, located in the Carr Creek watershed (Ashby 1985). Groundwater movement is in a western direction and numerous springs occur throughout the watershed (Ashby 1985).

Eau Galle Reservoir (0.6 km²) is hypereutrophic (TSI_{Chlorophyll} = 66) and exhibits high summer epilimnetic concentrations of P (0.092 mg L-¹) and chlorophyll (37.2 mg m³; Barko *et al.* 1990). Multiple sources of internal P loading in the lake from accreted sediment derived from decades of watershed loading sustain productivity when external P loading is nominal (James and Barko 1993).

Water sampling and flow gauging stations were established on the Upper Eau Galle River at bridges near the headwaters at County Road E (EGR-4.3 km), 60th Avenue (EGR-12.7 km), County Road N (EGR-18.5 km), and near the entrance to Eau Galle Reservoir (EGR-26.3 km). At each station, stage height was recorded at 15-min intervals (ISCO Model 730 bubbler module or Model 4120 pressure transducer; ISCO Inc., Lincoln, Nebraska). A stage-discharge relationship was determined over a variety of flow regimes to convert stage height to volumetric flow. Precipitation gauges (Model S-162; Dataloggers Inc.), placed near the gauging stations, monitored rainfall over 15-min intervals. Flows and precipitation were monitored between May and September, 2002.

During storm inflows, water samples were collected at short time intervals (15-30 min) with automated sampling equipment (ISCO 3700 or 6700 samplers), and composited into daily, flow-weighted samples for chemical analysis. In the laboratory, a portion of the sample was filtered onto glass fiber filters (Gelman Metricel; 2 μ nominal pore size) and dried at 105°C to a constant weight for determination of total suspended solids (TSS; APHA 1998). Another portion was filtered through a 0.45 μ m filter for soluble constituent determination. Soluble reactive P (SRP) was analyzed using automated analytical techniques (Lachat Quikchem Autoanalyzer, Hach Company, Lachat Div., Loveland, Colorado). Total and total soluble P were analyzed colorimetrically

using Lachet QuikChem procedures following digestion with alkaline potassium persulfate according to Ameel et al. (1993). Additional sample was filtered onto a glass fiber filter (but not dried) for determination of labile and refractory forms of PP in the runoff. Sequential fractionation of PP was conducted according to Hieltjes and Lijklema (1980) and Nürnberg (1988) for the determination of ammoniumchloride-extractable PP (i.e., loosely-bound PP), bicarbonate-dithionite-extractable PP (i.e., iron-bound PP), sodium hydroxide-extractable PP (i.e., aluminum-bound PP), and hydrochloric acid-extractable PP (i.e., calcium-bound PP). A subsample of the sodium hydroxide extract was digested with potassium persulfate to determine nonreactive sodium hydroxide-extractable PP (Psenner and Puckso 1988). Labile particulate organic/polyphosphate PP was calculated as the difference between reactive and nonreactive sodium hydroxide-extractable PP. PP remaining on the filter after the hydrochloric acid extraction was digested with potassium persulfate and 5 N sulfuric acid (APHA 1998) for determination of refractory organic PP. Each extraction was filtered through a 0.45 µm filter, adjusted to pH 7, and analyzed for SRP using the ascorbic acid method (APHA 1998).

To measure P sorption characteristics of TSS loads, the remaining composited sample was centrifuged at 500 g and decanted to separate particulate sediment from soluble phases. Sediment aliquots (~500 mg L-1 dry weight equivalent) were subjected to a series of SRP (KH₂PO₄ as SRP) standards ranging from 0 to 1.0 mg L^{-1} (i.e., 0, 0.125, 0.250, 0.500, and 1.00 mg L⁻¹) for examination of P adsorption and desorption over a twenty-four hour period. The equivalent dry mass concentration used in the sorption assays fell within the range of TSS concentrations measured during storm runoff in the watershed. Untreated tap water (groundwater) from the laboratory was used as the water medium because it was phosphate-free and exhibited very similar cationic strength, conductivity, and pH to that of surface water from the Eau Galle River. Chloroform (0.1%) was added to inhibit biological activity. The assay systems, containing TSS, tap water, and known concentrations of SRP, were shaken uniformly for 24 hours; then sampled and analyzed for SRP. The assay systems were maintained under oxic conditions at a pH of ~ 8.0 to 8.3 and a temperature of $\sim 20^{\circ}$ C during shaking.

The change in SRP mass (*i.e.*, initial SRP - final SRP; mg) over the 24 hour period was divided by the dry mass equivalent of TSS used in the experiment to determine the quantity of P desorbed or adsorbed (mg P kg⁻¹ sediment). These data were plotted as a function of the equilibrium SRP concentration after 24 hours of incubation to determine the linear adsorption coefficient (K_d ; L kg⁻¹), the equilibrium P concentration (EPC; mg P L⁻¹; the point where net sorption is zero), and the native adsorbed P (S_o ; mg P kg⁻¹ sediment; initial P adsorbed to the sediment). The K_d and S_o were calculated via regression analysis as the slope and the y-

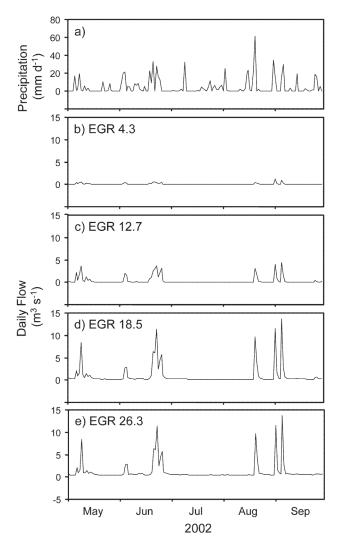


Figure 2.-Variations in mean daily precipitation (a) and flow (cms; cubic meters per second) at Upper Eau Galle River (EGR) kilometers 4.3 (b), 12.7 (c), 18.5 (d), and 26.3 (e) between May and September, 2002.

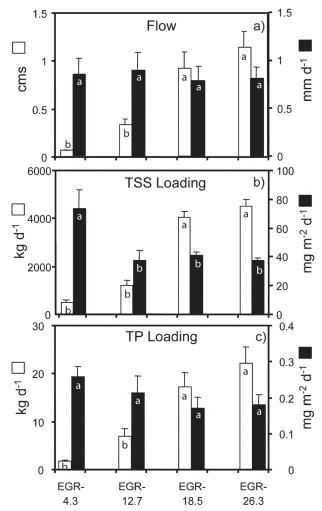


Figure 3.-Mean flow and areal runoff (a), total suspended solids (TSS, b), and total phosphorus (TP, c) loading (kg d⁻¹) between May and September, 2002, at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Areal export rate estimates (mg m⁻² d⁻¹) are weighted with respect to watershed area above each sampling station. Vertical lines above bars represent 1 standard deviation. Different letters between stations represent significant differences (p < 0.05) in means based on ANOVA (SAS 1994).

intercept, respectively, from linear relationships between final SRP concentrations and the quantity of P sorbed at low equilibrium concentrations (Pant and Reddy 2001). The EPC was calculated as $S_{\rm o}$ divided by $K_{\rm d}$.

Summer constituent loading rates and flow-weighted concentrations were determined using the software program FLUX (Walker 1996). Constituent loading was calculated either as the product of a flow-weighted average concentration and mean flow over different flow strata or by linear regression analysis of concentration versus flow. Constituent loading and flow at individual stations were also normalized with respect to the watershed area above each station for estima-

tion of areal export rates and runoff as a function of increasing watershed area.

Results

The Upper Eau Galle River responded to several storm events during summer, 2002, with peaks in flow along its longitudinal axis (Figure 2). Peaks in flow occurred in early May, early and late June, mid-August, and late August through early September. Flows were near nominal during a dry period between July and early August.

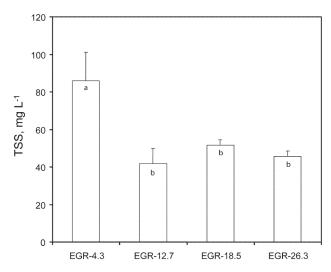


Figure 4.-The mean, flow-weighted, concentration of total suspended solids (TSS) between May and September, 2002, at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Vertical lines above bars represent 1 standard deviation. Different letters between stations represent significant differences (p < 0.05) in means based on ANOVA (SAS 1994).

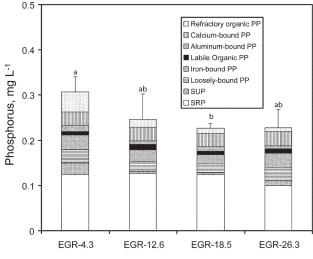


Figure 5.-The mean, flow-weighted, concentration of total phosphorus and phosphorus species between May and September, 2002, at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. PP = particulate phosphorus; SUP = soluble unreactive phosphorus; SRP = soluble reactive phosphorus. Vertical lines above bars represent 1 standard deviation for the mean total phosphorus concentration. Different letters between stations represent significant differences (p < 0.05) in mean total P based on ANOVA (SAS 1994).

Mean daily flow was lowest at EGR-4.3 and increased with increasing distance from the headwaters (Figure 3). Flow increased considerably between stations EGR-12.7 and EGR-18.5 due to inflows from Carr Creek. Abrupt increases in TSS and total P loadings also occurred at EGR-18.5 (Figure 3), indicating loading influences from Carr Creek. In contrast, loading changes for these constituents were much smaller between EGR-4.3 and EGR-12.7 and between EGR-18.5 and EGR-26.3. Although not statistically significant (t-test; SAS 1994), the sum of the loads originating from EGR-12.7 and Carr Creek were slightly greater than the load estimated at EGR-18.5 for TSS (5013 kg d⁻¹ versus 4065 kg d⁻¹, respectively) and total P (20.4 kg d⁻¹ versus 17.2 kg d⁻¹, respectively). This pattern suggested possible retention of a small portion of these loads in the flood plain upstream of EGR-18.5. Loads weighted with respect to unit watershed area above each station (i.e., areal export rates) were either greatest in the headwaters of the Upper Eau Galle River at EGR-4.3 (i.e., for TSS) or generally uniform between the four stations as a function of increasing watershed area (i.e., for total P; Figure 3). Similar patterns were observed when export and runoff rates were evaluated as a function of watershed area between each station (not shown).

Flow-weighted concentrations of TSS were greatest in the headwaters of the Upper Eau Galle River at EGR-4.3 (Figure 4). They declined downstream and were uniform between EG-12.7 and EGR-26.3, similar to patterns observed for

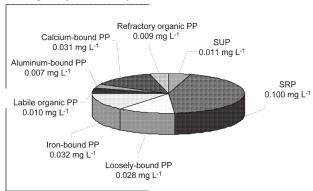
areal export rates. Station EGR-4.3 also exhibited greater concentrations of particulate P in the runoff compared to downstream stations (Figure 5). However, there were no statistically significant differences in concentrations of total P as a function of distance from headwaters.

Soluble forms of phosphorus (primarily as SRP) comprised between 48 and 57% of the flow-weighted concentration of total P over all stations (Figure 5). Labile forms of PP were dominated by the loosely-bound and iron-bound PP fraction while the refractory PP was primarily in the form of calciumbound PP. Station EGR-4.3 exhibited greatest concentrations of refractory organic PP compared to the other stations.

For Upper Galle River inflows entering Eau Galle Reservoir at EGR-26.3, 79% of the flow-weighted total P concentration was composed of labile P forms (*i.e.*, soluble P plus labile PP; Figure 6). Soluble P and labile PP forms accounted for 49% and 30% of the total P load, respectively. SRP, accounting for 44% of the total P load, is directly available for algal growth while phosphomonoesters (as a part of SUP) can be converted to ortho-P via enzymatic activity under P-limiting conditions (Franko and Heath 1979). Loosely-bound and iron-bound PP fractions, which comprised 86% of the labile particulate PP fraction (*i.e.*, 40% and 46%, respectively), can be recycled in receiving waters via equilibrium reactions, and eH and pH reactions (Mortimer 1971; James *et al.* 1996). Labile organic PP can be recycled via bacterially-mediated reactions (mineralization and enzymatic hydrolysis of poly-

Phosphorus Composition

Biologically-refractory PP



Biologically-labile PP

Figure 6.-Pie chart showing the percent composition and mean, flow-weighted, concentrations of various phosphorus (P) species for P loads at river kilometer 26.6 of the Upper Eau Galle River. Biologically labile particulate and soluble P forms accounted for 79 % of the total P concentration. Biologically labile particulate P forms represented 60% of the particulate P concentration. PP = particulate phosphorus; SUP = soluble unreactive phosphorus; SRP = soluble reactive phosphorus.

phosphate forms; Gächter et al. 1988; Gächter and Meyer 1993; Hupfer et al. 1995).

Mean P equilibrium characteristics of TSS loads indicated that considerable P desorption occurred at SRP concentrations less than ~ 0.15 mg L^{-1} for all stations (Figure 7). Adsorption of soluble P onto TSS occurred at high ambient SRP concentrations. The EPC was very high and similar to flow-weighted mean SRP concentrations determined over the summer period at each station (Figure 8), suggesting regulation of ambient SRP via equilibrium processes with TSS in the runoff. The linear adsorption coefficient was near 1000 L kg⁻¹ for all stations (Table 2), indicating a strong buffering capacity for ambient P under conditions of P disequilibrium.

Discussion

An important need for watershed model improvement is identification and prediction of biologically available forms of nutrients from field runoff in the watershed, its transport to receiving waters, transformations, recycling, and fate. Determination of only total and soluble P loading does not always provide sufficient information regarding the potential for recycling and biological uptake in receiving waters. For instance, Burns *et al.* (1976) estimated that 45% of the total P load entering Lake Erie was refractory apatite P, indicating that a substantial portion of the total P load was biologically

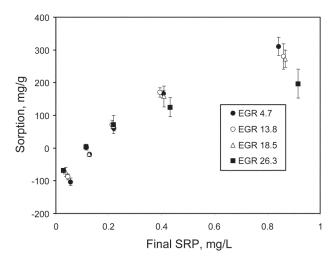


Figure 7.-Adsorption and desorption characteristics as a function of ambient soluble reactive phosphorus (SRP) concentration for total suspended solids collected during storm events at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Vertical lines indicate 1 standard deviation.

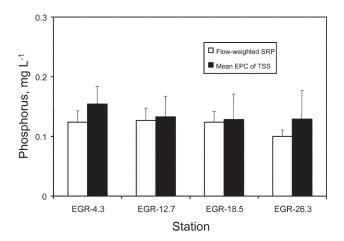


Figure 8.-A comparison of mean, flow-weighted, soluble reactive phosphorus (SRP) concentrations and the mean equilibrium phosphorus concentration (EPC) for total suspended solids (TSS) loads at Upper Eau Galle River (EGR) kilometers 4.3, 12.7, 18.5, and 26.3. Vertical lines indicate 1 standard deviation. No significant differences were found between flow-weighted SRP concentration and the EPC of TSS (t-test; SAS 1994).

Table 2.-Mean (\pm 1 S.E.) equilibrium phosphate concentration (EPC), linear adsorption coefficient (K_d), and native adsorbed phosphorus (S_o) for suspended solids runoff at various stations in the Upper Eau Galle River Watershed.

Station	EPC (mg L-1)	Kd (L kg ⁻¹)	So (kg L ⁻¹)
EGR 4.3	0.154 (0.010)	1017 (106)	159 (22)
EGR 12.7	0.133 (0.013)	981 (136)	126 (17)
EGR 18.5	0.128 (0.022)	777 (70)	101 (21)
EGR 26.3	0.129 (0.024)	791 (202)	88 (2)

unavailable for uptake. In this study, partitioning of total P into functional biologically labile and refractory components revealed that the loosely-bound and iron-bound PP fractions were important constituents of Upper Eau Galle River loads entering the reservoir. James and Barko (1997) found that greater than 50% of the P loading originating from the Eau Galle River watershed is retained as deposited sediment in the reservoir. Internal P loading from both profundal and littoral sediments in the reservoir, driven by eH and pH reactions, is high (range= 3.2 to 8.1 mg m⁻² d⁻¹; James and Barko 1993), and believed to be driven primarily by iron-phosphorus associations and ligand exchange mechanisms (James et al. 1990; James and Barko 1991). Thus, knowledge of loading and storage of loosely-bound and iron-bound PP to this as well as other aquatic systems, and management to reduce these inputs would be critical in future water quality improvement of the reservoir. Watershed models that identify critical source areas (i.e., nutrient source areas in the landscape that are sensitive to runoff and exhibit connectivity to a tributary; Gburek and Sharpley 1998; Walter et al. 2000, 2001) and predict source inputs of these (and other) labile PP fractions as a function of land use practice would be valuable in the development and implementation of BMPs to reduce runoff to receiving waters that are biologically responsive to these constituent inputs.

A significant finding of this study was the occurrence of high concentrations of SRP in the runoff along the watershed's longitudinal axis and an apparent link to equilibrium processes between TSS and aqueous phases. Sharpley et al. (1993) suggested that preferential transport of clays, coupled with P adsorption-desorption processes, could increase (or decrease) the bioavailability of P as loads moved through the watershed, depending on equilibrium relationships between solid and aqueous phases. In the Upper Eau Galle River watershed, surface soil P is heavily subsidized with manure and fertilizer inputs in agricultural areas, resulting in very high mean crop-available P concentrations ranging between 120 and 180 ppm (as Mehlich-3 P; James unpublished data). James et al. (2004) found that the EPC and S_o of TSS in field runoff of various land uses within the Upper Eau Galle River watershed increased as a function of increasing P management of the landscape (i.e., livestock containment areas versus corn fields versus woodlots). This pattern indicated that binding sites on soils were becoming more saturated with P in managed areas of the landscape, resulting in higher EPC and greater P desorption potential under conditions of P disequilibrium (Ruiz et al. 1997). The EPC for TSS loads in the Upper Eau Galle River was high (> 0.1 mg L⁻¹) relative to other studies (Meyer 1979; Mayer and Gloss 1980; Froelich 1988; Olila and Reddy 1993), which reflects soil fertility management practices in the watershed (i.e., fertilizer and manure subsidies). The strong correspondence between flow-weighted SRP concentrations along the longitudinal axis of the watershed and the EPC of the TSS indicated that equilibrium processes, derived from agricultural soil erosion, were largely regulating SRP concentrations as constituent loads move downstream.

With the exception of the headwaters, longitudinal concentration gradients for P constituents were minor, indicating a homogeneous land-use mosaic throughout most of the watershed. In particular, concentrations of most constituents were diluted as loads moved downstream, indicating that hydrologic runoff was increasing at a faster rate than constituent runoff over the longitudinal axis of the watershed and/or some temporary retention of constituent loads (via sedimentation) was occurring along the floodplain. In contrast to these patterns, longitudinally increasing constituent concentrations and export rates could signify changes in land use (*i.e.*, increased soil management or urban runoff) and/or erosion of floodplain material.

Our results indicated that biologically labile PP forms (particularly loosely-bound and iron-bound PP), in addition to soluble P, need to be considered in TMDL estimation, P index analysis, and watershed-receiving water models for improved forecasting and evaluation of management scenarios to reduce P runoff to lakes and impoundments. Transport management strategies such as tilling nutrient amendments into the soil shortly after application, constructing buffer strips adjacent to critical source areas, planting perennial cover, contouring, conservation tillage, and wetland rehabilitation would be needed to reduce erosion of biologically labile PP and slow its runoff to receiving waters by promoting interception and trapping (Sharpley et al. 1999, Gburek et al. 2000). Additionally, equilibrium processes between TSS and aqueous phases can result in very high SRP concentrations in the runoff due to P desorption from particles for agriculturally-managed watersheds like the Upper Eau Galle River. Thus, both source and transport control practices that achieve overall reductions in soil P concentration (i.e., modifying or abating P amendments and allowing crop uptake to deplete concentrations over a period of years) in critical source areas would be needed in order to effect a change in the EPC between particulate and aqueous phases.

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